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SPECIFICATION

1. Title of the Invention

Screen Printing Ink and Process for Screen Polychrome Printing

2. Claims

(1) A UV and electron ray curable screen printing ink essentially containing at least one polymerizable low-molecular material selected from monomers, oligomers or prepolymers, each having in its molecule a polymerizable functional group selected from acryloyl, methacryloyl and allyl groups, photopolymerization initiator and colouring agent.

(2) A screen printing ink of claim 1 which has a viscosity of 10 to 200 poise.

(3) A process for screen polychrome printing comprising the steps of:

subjecting a substrate to a screen printing with a UV and electron ray curable screen printing ink essentially containing at least one polymerizable low-molecular material selected from monomers, oligomers or prepolymers, each having in its molecule a polymerizable

functional group selected from acryloyl, methacryloyl and allyl group, photopolymerizsation initiator and colouring agent,

curing the ink-surface by the irradiation of UV to such an extent that a subsequent printing step is operable,

thereafter repeating the screen printing at least one time with a UV and electron ray curable screen printing ink of different colour, a curing step of ink-surface by the UV irradiation being disposed between each screen printing step if two or more screen printings are repeated, and

then irradiating an electron ray after the last screen printing to completely cure the ink.

3. Detailed Description of the Invention

The present invention relates to an improvement in a technology of screen printing by the use of UV and electron ray curing, in particular, to a UV and electron ray curable screen printing ink and a process for screen printing by the use of it.

A screen printing is widely employed for advertisement media such as poster and display, manufacture of a variety of decorative products, picturing of glass, ceramic materials and plastic containers, and so on. This printing is easy in its operation and the printing machine and plate are both rather cheap. In addition, it has an advantage that a thick ink printing is possible, whereby a printing of highly attractive design may be obtainable. On the contrary, the printing ink contains a solvent of high boiling point to prevent a clogging of plate, and further the thick ink printing renders the drying of ink after printing troublesome. It is necessary for complete drying to let the printed matter alone for a long period of time at an ambient temperature, or alternatively a large scale furnace for heat drying is indispensable for the short time drying. Furthermore, when the printing of different colour is repeated, it is as well indispensable to dry the ink every one colour printing (to such an extent that at least no obstruction is caused for the subsequent printing step.)

The inventors of the present application researched to radically solve the issues mentioned in the above and succeeded in developing a UV and electron ray curable screen printing ink. Since the drying and curing of ink is feasible in a moment by irradiating

UV or electron ray, the conventional drying step can be avoided and a polychrome printing may be completed in a short time of period.

A screen printing ink of the present invention essentially contains at least one polymerizable low-molecular material selected from monomers, oligomers or prepolymers, each having in its molecule a polymerizable functional group selected from acryloyl, methacryloyl and allyl group, photopolymerization initiator and colouring agent.

The term "low-molecular material" herein defined means to oppose the term "high-molecular material", and encompasses not only monomers having polymerizable functional group but also oligomers as defined to be a polymerized product of several monomers and prepolymers which is a polymerized product of much more monomers but provided with properties similar to a monomer as compared to a high-molecular material. As the distinction of polymer and prepolymer, a general boundary to treat as a high-molecular material or not, approximately molecular weight of about 10,000, may be suitable in this invention.

The low-molecular materials having in their molecules acryloyl group as the polymerizable functional group are exemplified below.

(Acrylate Monomers)
Methylacrylate, ethylacrylate, n-butylacrylate, isobutylacrylate, 2-ethylhexylacrylate, isodecylacrylate, laurylacrylate, stearylacrylate, 2-hydroxyethylacrylate, 2-hydroxypropylacrylate, trimethylolpropane triacrylate, methoxyethylacrylate, n-butoxyethylacrylate, dimethylaminoethylacrylate, diethylaminoethylacrylate, ethyleneglycol diacrylate, propyleneglycol diacrylate, neopentylglycol diacrylate, 1,6-hexanediol diacrylate, diethyleneglycol diacrylate, triethyleneglycol diacrylate, dipropyleneglycol diacrylate, ethylcarbitolacrylate, 1,5-pentanediol diacrylate, pentaerythritol triacrylate, dipentaerythritol pentaacrylate, dipentaerythritol hexaacrylate, tetrahydrofurfurylacrylate, glycidylacrylate, dibenzylacrylate, 2-hydroxyethylacryloyl phosphate, etc.

(Acrylate Oligomers)
2-Hydroxy-3-phenoxypropylacrylate,
α,ω-diacryloylbisethyleneglycol phthalate,
α,ω-diacryloylbisethyleneglycol tetrahydrophthalate,
α,ω-tetraacryloylbistrimethylolpropane tetrahydrophthalate,
α,ω-tetraacryloylbistrimethylolpropane tetrahydrophthalate, etc.

(Oligomers and Prepolymers)
Epoxyacrylate, polyester type urethane acrylate, polyether type urethane acrylate, melamineacrylate and other oligomers and prepolymers of various acrylates.

The polymerizable low-molecular material having methacryloyl group are exemplified below.

(Methacrylates of Low-molecular Alcohols)
Methylmethacrylate, ethylmethacrylate, n-butylmethacrylate, isobutylmethacrylate, 2-ethylhexylmethacrylate, isodecylmethacrylate, laurylmethacrylate, stearylmethacrylate, 2-hydroxyethylmethacrylate, 2-hydroxypropylmethacrylate, dimethylaminomethacrylate, diethylaminoacrylate, ethyleneglycol dimethacrylate, diethyleneglycol dimethacrylate, triethyleneglycol dimethacrylate, trimethylolpropane trimethacrylate, tetraethylneglycol dimethacrylate, 1,3-butanediol dimethacrylate, tetrahydrofurfuryl methacrylate, glycidylmethacrylate, etc.

(Methacrylates of Various Oligomers or Prepolymers)
Polyester methacrylate, epoxy methacrylate, urethane methacrylate, polyether methacrylate, polyol methacrylate, melamine methacrylate, etc.

The polymerizable low-molecular materiel having allyl group are exemplified below.

Diallylidenepentaerithritol, triallyl isocyanate, diallyl phthalate, trimethylolpropane diallyl ether, etc.

The above-mentioned polymerizable low-molecular material may be used by mixing two or more of them, and such mixing is preferable. The film formed by the ink cure generally changes from

soft to hard in accordance with the increase in the number of functional groups present in the basic unit of the polymerizable low-molecular material. If a soft cured film is desirable, a mixture of main component having 1 to 2 functional groups is preferably used. On the other hand, if a hard cured film is desired, a mixture of main component having 3 or more functional groups is preferably used.

These polymerizable low-molecular materials constitute a printing ink of the invention as a main vehicle ingredient together with a colouring agent and other optional ingredients hereinafter mentioned. The quantity of the polymerizable low-molecular material is admixed so as to occupy 5% by weight or more of the ink composition. If the quantity of the polymerizable low-molecular material is of less than 5%, the film of the printing ink cured by the action of the electron ray irradiation is weak and cause troubles such as insufficient friction-resistance. The preferred quantity to be admixed is of more than 20%.

A colouring agent includes dyes and pigments which are conventionally included into the printing ink and there is no specific limitation. For instance, a variety of dyes such as diperse dye, cationic dye, acid dye and direct dye are all preferably used. Also preferable are a variety of pigments such as Titanium White, Carbon Black, Prussian Blue, Red Iron Oxide, Ind. Yellow G, Benzidine Yellow G, Pyrazolone Orange, Vulcan Orange, Brilliant Fast Scarlet, Pyrazolone Red, Watchung Red, Lithol Red R, Lake Red, Brilliant Carmine 3B, Brilliant Carmine 6B, Lake Bordeaux 2R, Rhodamine 6G and Phthalocyanine Blue.

These colouring agents may be admixed to the printing ink by the quantity of upto 50%, preferably in the range of 1 to 30%.

The photopolymerization initiator acts to polymerize the polymerizable low-molecular material upon receiving an irradiation of UV ray and form a cured film at least the surface of the printed ink. Any photopolymerization initiator may optionally used if it creates a radical by the UV irradiation. Those accompanying no colour change nor coloring are preferred. For example, benzoin ethers such as benzoin methyl ether, benzoin isopropyl ether, benzoin-n-butyl ether and benzoin-i-butyl ether, benzophenones, halogenated acetophenones

and biacetyls are exemplified. These photopolymerization initiators are usually admixed to the ink composition so as to occupy 5 to 10% thereof.

The screen printing ink of the invention may be supplemented with aids such as wax, stabilizer, antifoaming agent, leveling agent, antisagging agent, etc., if necessary. The viscosity of ink should be maintained in the range of 10 to 200 poise, preferably, 10 to 100 poise so as to obtain optimal printing properties. (The viscosity value was measured at a temperature of 20°C.) The method to prepare the printing ink by admixing several ingredients may follow the conventionally established technique in this art.

The present invention, as stated in the foregoing, also relates to a process for polychrome printing by the use of the screen printing ink mentioned above. The process for screen polychrome printing in accordance with the present invention comprises the step of:

subjecting a substrate to a screen printing by the use of the above-mentioned UV and electron curable screen printing ink essentially containing at least one polymerizable low-molecular material selected from monomers, oligomers or prepolymers, each having in its molecule polymerizable functional group selected from acryloyl, methacryloyl and allyl group;

curing the ink surface by the irradiation of UV ray to such a degree of "dryness to touch" that a subsequent printing step is operable;

thereafter repeating the screen printing at least one time with a UV and electron ray curable screen printing ink of different colour, a curing step of ink-surface by the UV irradiation being disposed between each screen printing step if two or more screen printings are repeated; and

then irradiating an electron ray after the last screen printing to completely cure the ink.

The printing machine may be of any type such as platen printing machine and rotary screen printing machine.

The printing may be carried out on any substrate such as paper, fabrics, plastic sheet, metal plate, glass, ceramics, inorganic board, etc.

The UV may be irradiated by, for instance, high pressure mercury lamp of 50 to 200 W/cm, one to ten lamps being arranged if necessary.

A device for irradiating the electron ray and its operative conditions are subsequently illustrated below for curing the printed ink. By means of a low energy electron ray accelerator, for example, Electrocurtain CB 200/50/30 supplied by Energy Science Co., Ltd. or NP-ESH 150 manufactured by Otto-Duel Corp. under the conditions of acceleration potential 100 to 300 KV and irradiation current 0 to 100mA, an electron ray of 0.5 to 30 Mrad is irradiated in the atmosphere of nitrogen gas.

According to the present invention, the screen printing ink is cured in a moment at least in its surface by the UV irradiation and in whole by the electron irradiation , and so the conventional drying step can be avoided, whereby the screen polychrome printing is provided with an extremely speed up. The space of the working area is therefore not occupied for a long period of time and the energy consumption is also extremely shortened.

Another big advantage is that since both of UV and electron ray curing are of low temperature curing, plastic films easily softened and papers easily shrinked by heat drying are employed without any obstruction as a printing substrate. The positioning operation indispensable to the polychrome printing is feasible without any problem.

If an ink-diluting agent of high boiling reactive monomer is selectively used, there is no problem of plate clogging and the washing of plate is easy. The printing operability is enormously high.

Example 1

The following ingredients (% by weight) were admixed in a pre-mixer to prepare colour pastes of four colours, followed by

subjecting to a mill of three rolls to obtain four kinds of screen printing inks.

"Lipoxy" VP 90 (epoxyacrylate manufactured by Showa Kobunshi)		5 parts
"Allonix" M5700 (oligoester acrylate manufactured by Toa Gosei)		80 parts
Benzophenone		5 parts
Hydroquinone monomethyl ether		0.5 parts
Colouring agent:	First titanium white	20 parts
	Second red iron oxide	15 parts
	Third Prussian blue	15 parts
	Fourth carbon black	15 parts

The viscosity of the printing ink was adjusted to approximately 20 poise by attritor. A printing substrate of polyethylene terephthalate film (manufactured by Toray, "Lumilar", 16 μm in thickness) was subjected to a rotary screen printing machine (manufactured by Stoke) and four screen printings were repeated at a printing rate of 50m/min.

After each one colour printing, a UV ray from double lamps of Highcure Lamp of 80 W/cm manufactured by Nippon Batteries was irradiated to dry the ink to the extent of dryness to touch. After the completion of the fourth colour printing, an electron ray from Electrocurtain CB 200/50/30 manufactured by Energy Science was irradiated onto the ink surface in an atmosphere of nitrogen gas to completely cure it.

Example 2

The following ingredients were admixed to obtain screen printing inks of two colours.

"Allonix" M6300 (methacrylate manufactured by Toa Gosei)	10 parts

Trimethylolpropane trimethacrylate		70 parts
Benzophenone		10 parts
Colouring agent:	First titanium white	20 parts
	Second carbon black	15 parts

The ink viscosity was arranged to be about 90 poise, and a printing substrate of asbestos slate (provided with a white under coating) in size of 3×6 *Shaku* was subjected to a new long type semi automatical printing machine to carry out the screen printings.

After the first colour printing, a UV ray was irradiated as in Example 1 to dry to the extent of dryness to touch, and after the second colour printing, an electron ray was irradiated under the same conditions as in Example 1 to obtain a completely cured ink.